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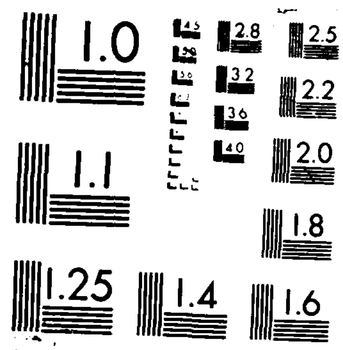

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FTD-ID(RS)T-0803-87

FOREIGN TECHNOLOGY DIVISION

USING BINARY MIXTURES OF VINYL MONOMERS FOR SYNTHESIZING CELLULOSE GRAFT COPOLYMERS

by

G.I. Stanchenko, R.M. Livshits, Z.A. Rogovin

HUMAN TRANSLATION

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Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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USING BINARY MIXTURES OF VINYL MONOMERS FOR SYNTHESIZING CELLULOSE GRAFT COPOLYMERS

G. I. Stanchenko, R. M. Livshits, Z. A. Rogovin

The possibility of giving modified cellulose fibers a set of new commercially valuable characteristics can obviously be greatly expanded by grafting from binary mixtures of monomers [1]. Moreover, grafting from a binary mixture of monomers is of considerable scientific interest, especially for explaining the kinetic characteristics of this reaction. (page 2)

This article gives the results we obtained when studying this problem.

Experimental Part

The graft copolymers were synthesized using the same procedure as in the ordinary method of grafting by chain transfer from initiator radicals in a block and an aqueous emulsion. The source materials were

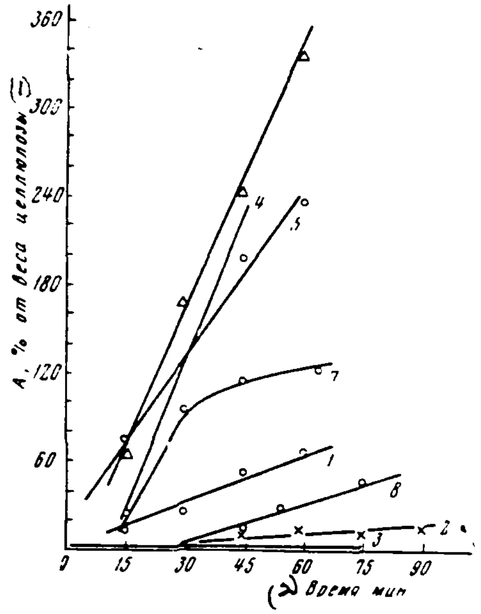
viscose staple fibers. In order to remove the homopolymers, the graft copolymerization products obtained were extracted by the appropriate solvents. The composition of the grafted chains was calculated according to the quantity of the graft polymer and the element analysis of the products obtained.

In order to determine the degree of swelling, transverse cross sections of fibers 10-15 mm thick were sketched under a microscope before and after swelling at 20°. The degree of swelling (%) was determined from the change in the cross-sectional area of the fiber

$$\text{Degree of swelling} = \frac{S_{\text{наб}} - S_{\text{сух}}}{S_{\text{сух}}} \cdot 100.$$

Results and Their Discussion

Figures 1 and 2 give data describing the effect of the nature of the comonomers and their relationship in the source mixture of monomers on the graft copolymerization rate. It is evident from the data provided that when acrylonitrile (AN) is added to styrene (St), vinyl acetate (VA) and methyl acrylate (MA) or vinylidene chloride (VDC) is added to MA, we see a synergistic effect. Thus, for example, when the reaction is carried out for 60 minutes, 68% of pure AN and 7.2% of pure St are grafted to the viscose staple fiber, whereas 235% of the mixture of AN with St (63.5% of AN) is grafted under the same conditions. There is no synergistic effect when mixtures of AN and VDC or St and MA are used. The graft copolymerization rate of the mixture of St with MA is close to the additive value, and that of AN with VDC - even somewhat lower than the additive value. Report [2] comments about the marked increase in the photoinitiated grafting rate of a mixture of NA with St on cellophane film over grafting of each monomer individually. Similar results were obtained during radiation grafting of these monomers on a viscose cord [3]. An increase in the rate of radiation grafting on



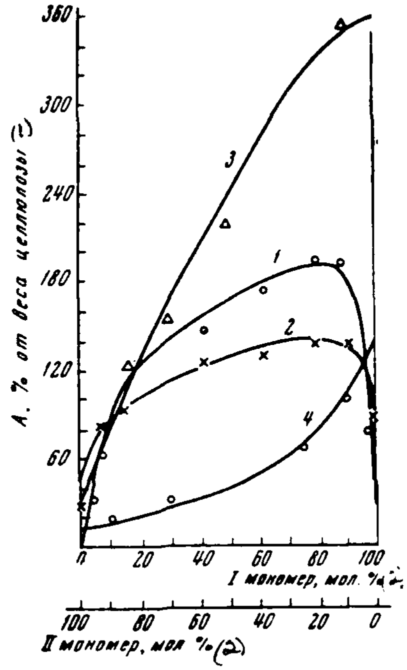


Fig. 1. Effect of reaction time on quantity of graft polymer. Grafting was carried out in a block using ammonium persulfate [6]. Reaction conditions: $[(NH_4)_2S_2O_8]$ = 0.01 g/g of fiber, 60, modulus 50.

1 - AN; 2 - St; 3 - VA; 4 - MA; 5 - AN + MA (63.5 mol.% AN); 6 - AN + MA (63.5 mol.% AN); 7 - AN + VA (63.5 mol.% AN); 8 - St + MA (36.5 mol.% St). A - quantity of graft polymer.
KEY: (1) % of weight of cellulose. (2) Time, min.

Fig. 2. Effect of composition of source monomer mixture on quantity of graft polymer. See Fig. 1 for block reaction conditions; grafting in an aqueous emulsion was carried out on the system cellulose - Fe^{2+} - H_2O_2 [7]: $[H_2O_2]$ = 0.005%; total monomer concentration of 10.2%; 60°, modulus 50, emulsifier 0.2% (alkamon OS-20).
1 - AN + St (in block); 2 - AN + St (emulsion); 3 - VDC + MA (in block); 4 - AN + VDC (emulsion). A - quantity of graft polymer.
KEY: (1) % of weight of cellulose. (2) ... monomer, mol.%.

cellulose and polyvinyl alcohol fibers is also observed when butadiene is added to St and AN, and AN to St [4]. However, no synergistic effect is observed during radiation grafting of the mixtures St - methyl methacrylate (MMA), α-methyl styrene - MMA and Va - St to a viscose cord filament [3].

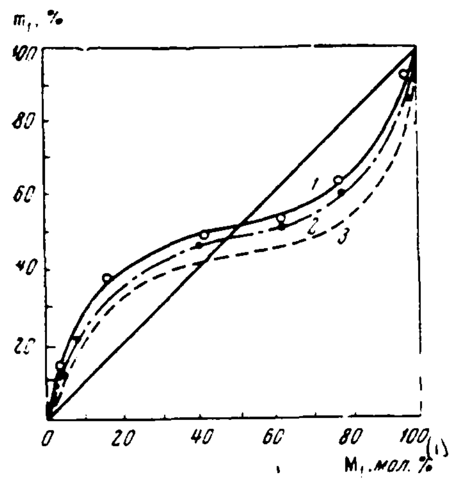


Fig. 3. Curves of composition of copolymer AN + St: 1 - graft copolymer; 2 - ungrafted copolymer formed during grafting; 3 - statistical copolymer according to data in [8]. See Fig. 1 for reaction conditions. M_1 - AN conent in source mixture of monomers, m_2 - AN content in copolymer. KEY: (1) mol.%.

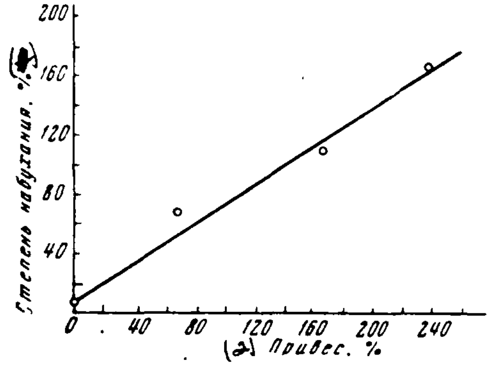


Fig. 4. Dependence of degree of swelling of cellulose fibers modified by grafting of mixture St - AN on quantity of graft copolymer. Swelling was carried out in a mixture of St and AN (63.5 mol.% AN). Composition of grafted chain - 54.5 mol.% AN. KEY: (1) Degree of swelling. (2) Weight gain, %.

Typically, the composition of grafted chains differs somewhat from the composition of the statistical copolymer, both when the reactions are carried out in a block and in an aqueous emulsion (Fig. 3). When the mixture AN - St is grafted, the AN content in the grafted chain is somewhat higher than in the statistical copolymer. An increase in the AN content over the statistical polymer during radiation grafting of the mixture MN - St on cellulose was also observed [4]. Similar principles also hold when the mixture AN - St is grafted on polyethylene and polytetrafluoroethylene [5].

The above data about the presence of a synergistic effect during grafting of mixtures of some monomers compared to statistical compolymerization can be explained by considering the effect of the quantity of monomers located directly in the fiber on the graft copolymerization

rate. Actually, when polymers (AN, VDC) that do not swell in the reaction medium or their copolymers are grafted, the accessibility of the cellulose material decreases during the course of the reaction because the grafted chains are located in the low-ordered sections of the fiber. When mixtures of AN with St, VA and MA and VDC with MA are grafted, the grafted chains of these copolymers swell in the reaction medium and in this case, the accessibility of cellulose increases with the increase in the quantity of graft polymer. The increase in the quantity of graft polymer is due to the marked increase in the length of the grafted chains (table).

Table. Effect of (AN - St) monomer source mixture composition on quantity of graft polymer, effectiveness of grafting, composition and characteristic viscosity of grafted chain*.

(1) Содержание АН в исходной смеси, мол. %	(2) Привес, % от веса целлюлозы		(3) Эффективность прививки, %		(4) Содержание азота в привитой цепи **, %		(5) Характеристическая вязкость привитой цепи *** [η], дл/г	
	(6) прививка в блоке	(7) прививка в эмульсии	(6) прививка в блоке	(7) прививка в эмульсии	(6) прививка в блоке	(7) прививка в эмульсии	(6) прививка в блоке	(7) прививка в эмульсии
0,0	0,0	27,0	—	—	—	0,0	—	1,55
8,5	62,0	89,1	64,1	55,0	2,8	2,4	2,75	—
16,2	123,8	92,3	62,8	54,4	6,2	5,4	5,50	2,3
42,7	145,5	121,9	77,0	70,2	9,0	8,5	7,30	3,8
63,5	172,0	128,2	75,3	72,1	10,0	9,6	7,00	4,6
79,6	175,2	139,7	83,[illegible]	80,6	11,9	12,1	7,00	4,95
94,0	193,0	134,5	94,0	89,4	18,9	18,2	—	3,55
97,0	75,5	127,5	98,1	98,7	22,7	22,6	1,50	—
99,0	77,9	81,5	99,2	98,5	24,8	24,5	1,2	—
100,0	27,8	85,0	98,8	98,5	—	26,0	1,16	3,45

* For grafting conditions see Fig. 2.

** The grafted chains were isolated by the hydrolysis of cellulose according to procedure [9].

*** [η] was determined in dimethylformamide at 30°C.

KEY: (1) AN content in source mixture, mol.%. (2) Weight gain, % of weight of cellulose. (3) Effectiveness of grafting, %. (4) Nitrogen content in grafted chain**. (5) Characteristic viscosity of grafted chain*** [η], dl/g. (6) Block grafting. (7) Grafting in emulsion.

As the data given in Fig. 4 show, the degree of swelling of the modified fibers in the mixture of monomers (AN - St) and, consequently, also the quantity of monomers in the fiber considerably increase with the increase in the quantity of graft polymer (in this case, of copolymer AN with St). The variation in the monomer content in the fiber during the grafting process results from the difference in the quantity of graft polymer when the systems AN - St and AN - VDC are used. Additional research, which we are presently conducting, is necessary to explain the difference in the quantity of graft polymer when the systems AN - St and St - MA, whose copolymers swell in the reaction medium, are used.

The enrichment of the graft copolymer chain with acrylonitrile observed during grafting of the mixture AN - St over the statistical copolymer is obviously due to the fact that the diffusion rate of AN in the cellulose material containing the graft copolymer is higher than that of St, which increases the AN concentration in the mixture of monomers in the fiber.

Conclusions

1. Graft copolymerization of cellulose with binary mixtures of vinyl monomers by chain transfer from the initiator radicals was investigated.

2. It was shown that a marked synergistic effect occurs when mixtures of acrylonitrile + styrene, acrylonitrile + vinyl acetate and acrylonitrile + methacrylate are grafted. The quantity of graft copolymer is considerably higher than for each of the monomers individually. The composition of the acrylonitrile - styrene grafted chain differs from that of the static copolymer obtained under the same conditions.

3. These facts are explained.

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